Michigan PFAS Sampling at Air Monitoring Sites

Melissa Woodward, Jitka Becanova, Rainer Lohmann
Graduate School of Oceanography, University of Rhode Island
August 2022

Overview

Passive sampler bowl set-ups were deployed at 27 air monitoring locations by the Michigan Department of Environment, Great Lakes, and Energy (EGLE) and the University of Rhode Island to measure the air PFAS concentrations throughout the state. This report contains the results of the measured concentrations, along with details pertaining to the quality assurance and quality control (QAQC) of the project.

PUFs are used to sample both particles and gas-phase compounds, and air samplers are used for gas-phase compounds. PUF samplers are not sufficient alone for measuring the volatile PFAS, as they equilibrate too quickly (as discussed in the Ahrens et al. 2013 paper), which is why we add the novel air samplers. Using both samplers helps us look at both the ionic and volatile PFAS in the air. The air samplers are novel passive samplers that show promise in both indoor and outdoor environments for measuring PFAS in the air. They have been used in tandem with PE sheets in indoor settings as reported in Morales-McDevitt et al. 2021 and can conveniently be used as both active and passive samplers (which is useful for calculating sampling rates).

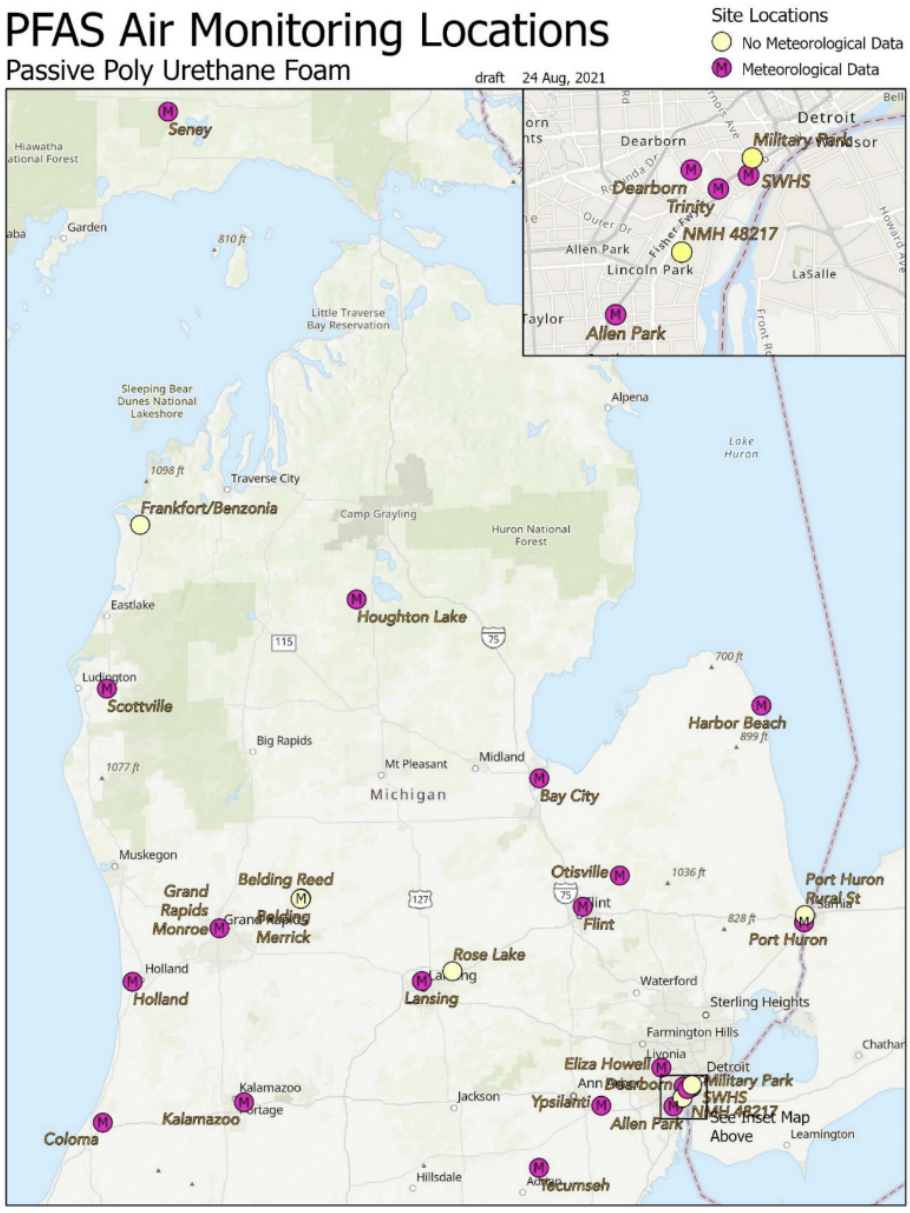
Sampler Information

43 air samplers and 43 PUF discs were sent to EGLE from URI. This included 4 field blanks and 6 travel blanks of each kind of sampler. 5 of the complete passive sampler set-ups were placed in one location for duplicate measurements. Two other sites had 2 complete set-ups also. Samplers were deployed late September 2022 (between 09/27 and 10/01) and collected late October 2022 (between 10/27 and 11/3). Samplers were deployed for a month (varying from 29 to 33 days depending on location) and sent back to URI on 11/04/2022 where they were extracted and analyzed. Sample deployment and collection procedures and site details can be found in the Quality Assurance Project Plan. Monitoring locations are shown on the map below.

PFAS Air Monitoring Locations

Passive Poly Urethane Foam

draft 24 Aug, 2021



Analyte	Type	Internal Standard
PFBA	Target	MPFBA
PFPeA	Target	M5PFPeA
PFHxA	Target	M5PFHxA
PFHpA	Target	M4PFHpA
PFOA	Target	M8PFOA
PFNA	Target	M9PFNA
PFDA	Target	M6PFDA
PFUnDA	Target	M7PFUdA
PFDoDA	Target	M2PFDoA
PFTrDA	Target	M2PFDoA
PFTeDA	Target	MPFTeDA
PFHxDA	Target	MPFTeDA
PFODA	Target	MPFTeDA
PFBS	Target	M3PFBS
PFPeS	Target	M3PFBS
PFHxS	Target	M3PFHxS
PFHpS	Target	M3PFHxS
PFOS	Target	M8PFOS
PFNS	Target	M8PFOS
PFDS	Target	M8PFOS
4:2 FTS	Target	M2-4:2FTS
6:2 FTS	Target	M2-6:2FTS
8:2 FTS	Target	M2-8:2FTS
FBSA	Target	MFOSA
FHxSA	Target	MFOSA
FOSA	Target	MFOSA
MeFOSA	Target	d-N-MeFOSA
EtFOSA	Target	d-N-EtFOSA
N-MeFOSAA	Target	d3-N-MeFOSAA
N-EtFOSAA	Target	d5-N-EtFOSAA
HFPO-DA	Target	M3HFPO-DA

Table 1: LCMS target compounds

Compound name	Description	Molecular Formula
6:2 FTOH	2-Perfluorohexyl ethanol	$C_8H_5F_{13}O$
8:2 FTOH	2-Perfluorooctyl ethanol	$C_{10}H_5F_{17}O$
10:2 FTOH	2-Perfluorodecyl ethanol	$C_{12}H_5F_{21}O$
N-MeFOSE-M	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	$C_{11}H_8F_{17}NO_3S$
N-EtFOSE-M	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	$C_{12}H_{10}F_{17}NO^3S$
N-MeFOSA-M	N-methylperfluoro-1-octanesulfonamide	$C_9H_4F_{17}NO_2S$
N-EtFOSA-M	N-ethylperfluoro-1-octanesulfonamide	$C_{10}H_6F_{17}NO_2S$
8:2FTAcr	1H, 1H, 2H, 2H-Perfluorodecyl Acrylate	$C_{13}H_4F_{17}O_2$
10:2FTAcr	1H, 1H, 2H, 2H-Perfluorododecyl Acrylate	$C_{15}H_7F_{21}O_2$

Table 2: GCMS target compounds.

Results

Location	***Corresponding label number of PUF/Air Sampler***
Flint- Whaley Park	FB01 ; 06
Bay City	FB02 ; 02
Houghton Lake	FB03 ; 16
Southwest High School	FB04 ; 22
Ypsilanti	FB05 ; 20
Grand Rapids- Monroe St	FB06 ; 13 ; 32
Holland	01
Frankfort / Benzonia	03
Coloma	04
Rose Lake	05
Otisville	07
Harbor Beach	08
Lansing	09 ; 33
Belding- Reed St	10
Belding- Merrick St	11
Kalamazoo	12
Tecumseh	14
Scottville	15
Port Huron- Dove Rd	17 ; 28 ; 29 ; 30 ; 31
Port Huron- Rural St	18
Seney	19
Allen Park	21
Dearborn	23
Eliza Howell-Road	24
NMH 48217	25
Trinity St. Marks	26
Military Park	27

Table 3: Site list with corresponding label number of sampler (e.g. 0921MI_Rad_27 and 0921MI_PUF_27 were deployed at Military Park).

Compound Detection at Sites

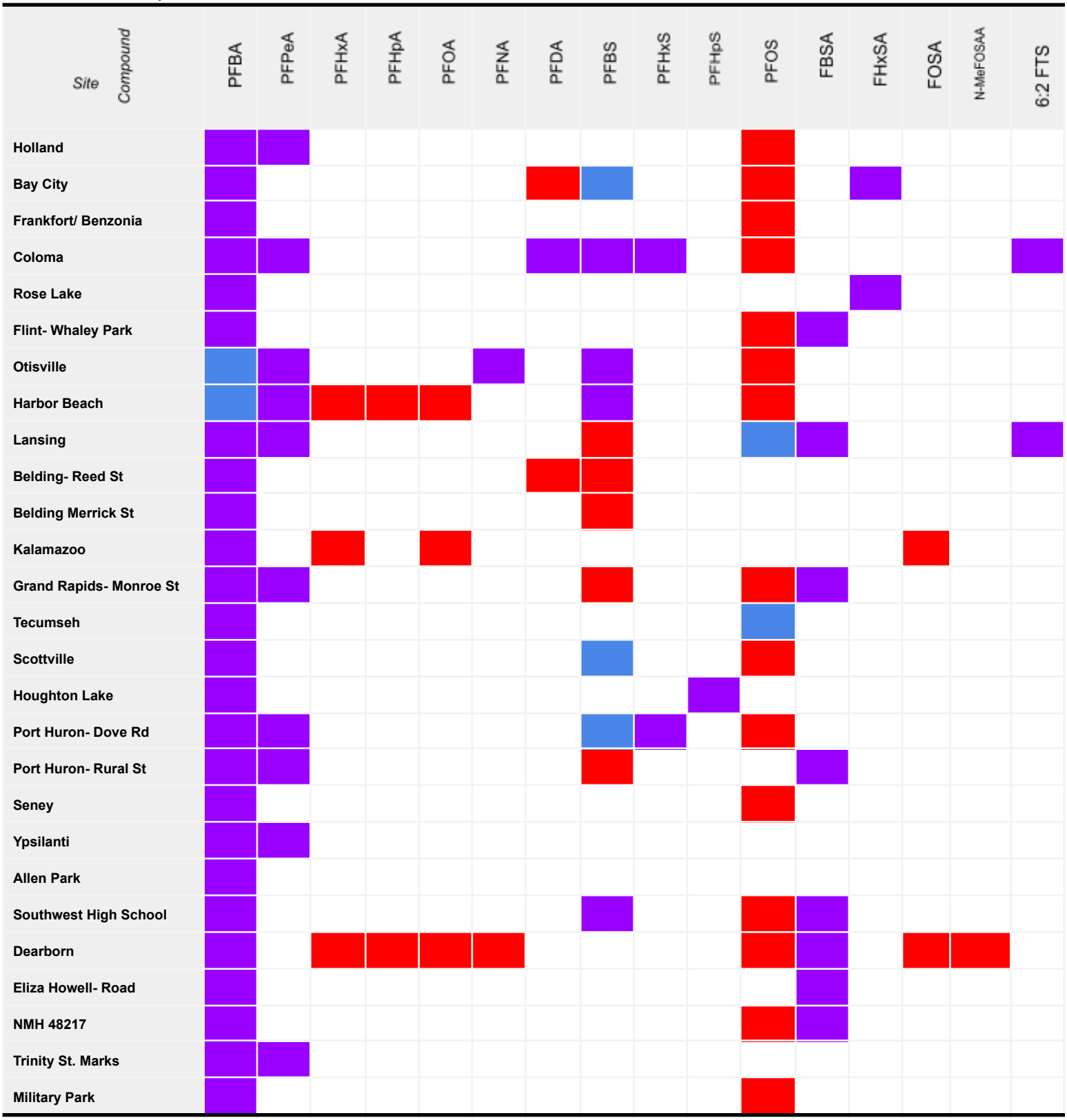


Table 4: Detection of ionic PFAS compounds by the samplers indicated by color code. Only compounds detected above detection limits in at least one of the samplers are listed. Purple = PUF, Blue = Both, Red = Air sampler.

Table 5: Detection of volatile PFAS compounds by the air samplers. Only compounds detected above detection limits are listed.

Detection Limits

	Instrumental Detection Limit (IDL)	Instrumental Quantification Limit (IQL)	Method Detection Limit (MDL) for PUF Samples	Method Detection Limit (MDL) for Air Samplers
PFBA	0.0099	0.0298	0.4285	0.3843
PFPeA	0.0068	0.0205	0.0510	0.0270
PFHxA	0.0010	0.0030	0.2538	0.0694
PFHpA	0.0006	0.0017	0.4681	0.0593
PFOA	0.0017	0.0052	1.7117	0.2513
PFNA	0.0014	0.0043	0.0919	0.0064
PFDA	0.0012	0.0035	0,0897	0.0063
PFUdA	0.0018	0.0053	0.1003	NC
PFDoA	0.0006	0.0017	0.1046	NC
PFTrDA	0.0002	0.0005	0.0494	NC
PFTeDA	0.0069	0.0208	NC	NC
PFBS	0.0050	0.0150	0.0979	0.0075
PFPeS	0.0019	0.0058	NC	NC
PFHxS Linear	0.0045	0.0136	0.0139	NC
PFHxS Branched	0.0234	0.0702	0.0351	NC
PFHpS	0.0034	0.0102	0.0090	NC
PFOS Linear	0.0074	0.0221	0.0641	0.0096
PFOS Branched	0,0143	0.0428	0.0464	0.0076
PFNS	0.0068	0.0205	NC	NC
PFDS	0.0076	0.0227	NC	NC
4:2 FTS	0.0120	0.0361	NC	NC
6:2 FTS	0.0002	0.0006	0.7974	NC
8:2 FTS	0.0006	0.0018	0.2963	NC
FBSA	0.0092	0.0277	0.0139	NC
FHxSA	0.0004	0.0012	0.0006	NC
FOSA	0.0014	0.0041	0.1979	0.0774
MeFOSA	0.0023	0.0070	NC	0.0674
EtFOSA	0.0054	0.0162	NC	NC
N-MeFOSAA	0.0069	0.0207	0.3233	0.0330
N-EtFOSAA	0.0042	0.0125	0.0900	NC
HFPO-DA	0.0027	0.0082	NC	NC

Table 6: Calculated IDL, IQL, and MDL for both PUF and air samplers from LCMS data for target ionic PFAS compounds. NC = Not Calculated. Units are ng.

The IDL and IQL for LCMS data, as shown in Table 6, were calculated using the signal to noise ratio of the lowest calibration point for each compound. As the same calibration points were used for both the PUF discs and air samplers, the IDL and IQL are calculated to be the same for both sampler sets. The MDL was generally calculated to be the blank average plus 3 times the standard deviation of the blanks, and so is specific to the compound and sampler type. Each sampler type data set consists of 4 travel blanks and 6 field blanks. For the PUF data set, both Field Blank 2 and Field Blank 6 were omitted from the MDL calculation. Where appropriate, outliers in the blank data set were replaced with half of the corresponding IQL. Samples were labelled as “<LOD" when their detected value was lower than the calculated MDL. Anything above the MDL has passed our QAQC standards.

	Method Detection Limit (MDL) for Air Samplers
6:2 FTOH	2.1963
8:2 FTOH	1.6946
10:2 FTOH	1.7366
EtFOSA	1.2357
MeFOSA	1.6065
MeFOSE	2.4183
EtFOSE	1.7363

Table 7: Calculated MDL for air samplers from GCMS data for target volatile PFAS compounds. NC = Not Calculated. Units are ng.

The MDL for GCMS data, as shown in Table 7, is individually calculated for each target compound as the blank average plus 3 times the standard deviation of the blanks. Samples below the MDL are labelled as “<LOD”.

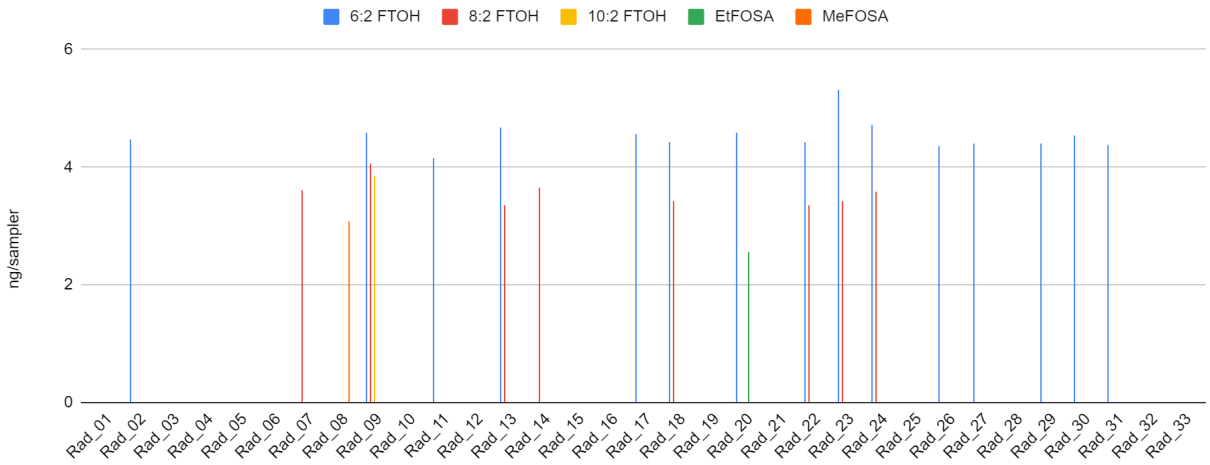


Figure 2: Measured volatile PFAS compounds in the air samplers reported in ng/sampler.

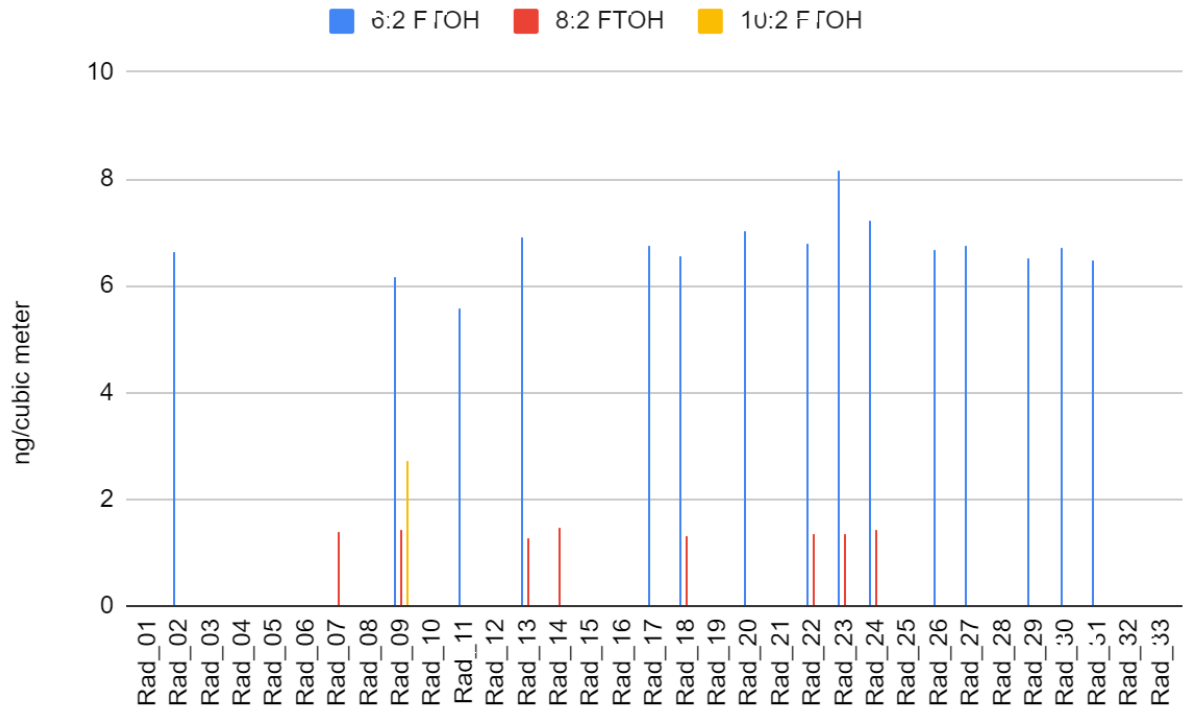


Figure 3: Calculated concentrations of volatile PFAS compounds in the air samplers reported in ng/m^3. Calculated concentrations for EtFOSA and MeFOSA are not reported as no sampling rate is available.

Figure 3 shows the concentrations of volatile PFAS compounds, reported as ng/cubic meter of air, measured in each air sampler. Calculated concentrations were done with previously determined sampling rates which are specific to the sampler and compound.
The most frequently detected compound is 6:2 FTOH, followed by 8:2 FTOH. 10:2 FTOH, MeFOSA, and EtFOSA were only detected in one sample each.

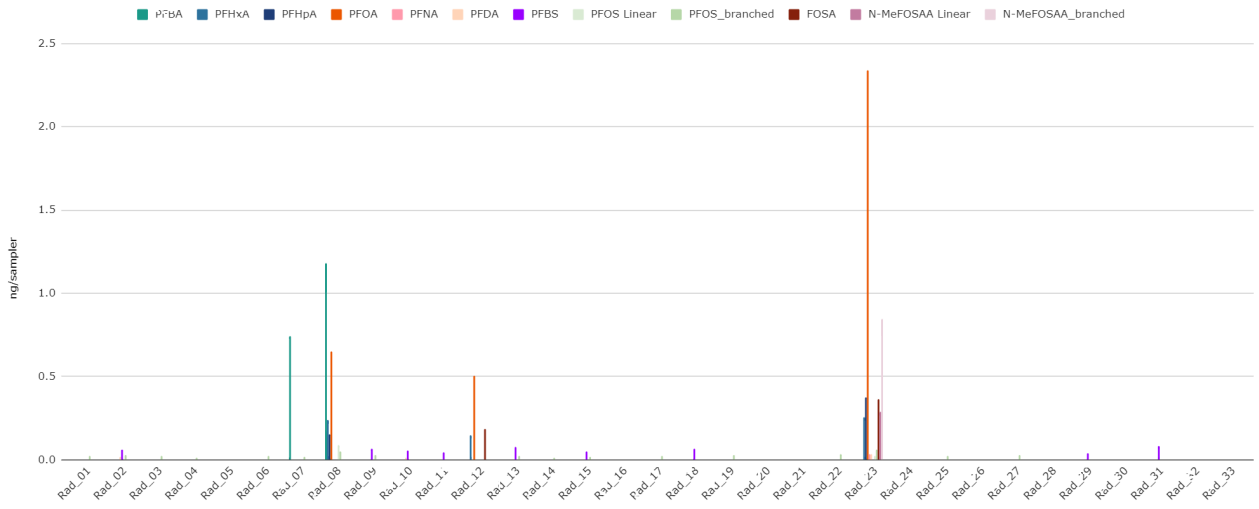


Figure 4: Measured concentrations of ionic PFAS compounds in the air samplers reported in ng/sampler.

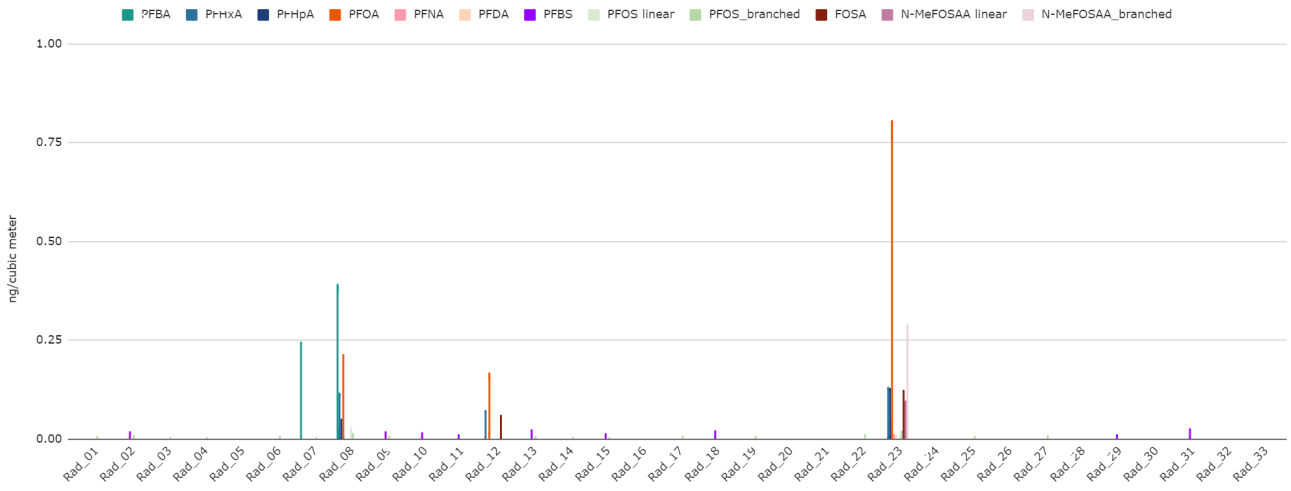


Figure 5: Calculated concentrations of ionic PFAS compounds in the air samplers reported in ng/m^3.

Figure 5 shows the concentrations of ionic PFAS compounds, reported as ng/cubic meter of air, measured in each air sampler. Calculated concentrations for PFHxA, PFBS, PFHpA, and PFDA were done with previously determined sampling rates which are specific to the sampler and compound. For the remaining detected compounds for which we did not have a specific air sampling rate for, an average sampling rate was used to estimate the concentrations in ng per cubic meter of air.

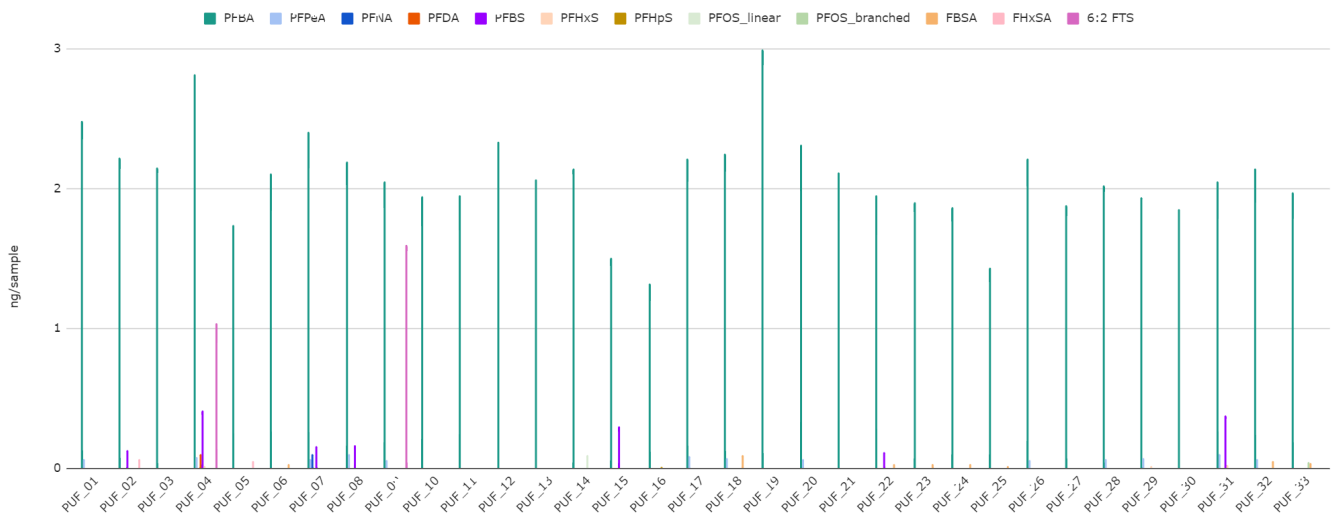


Figure 6: Measured concentrations of ionic PFAS compounds in the PUF disc samples reported in ng/sample.

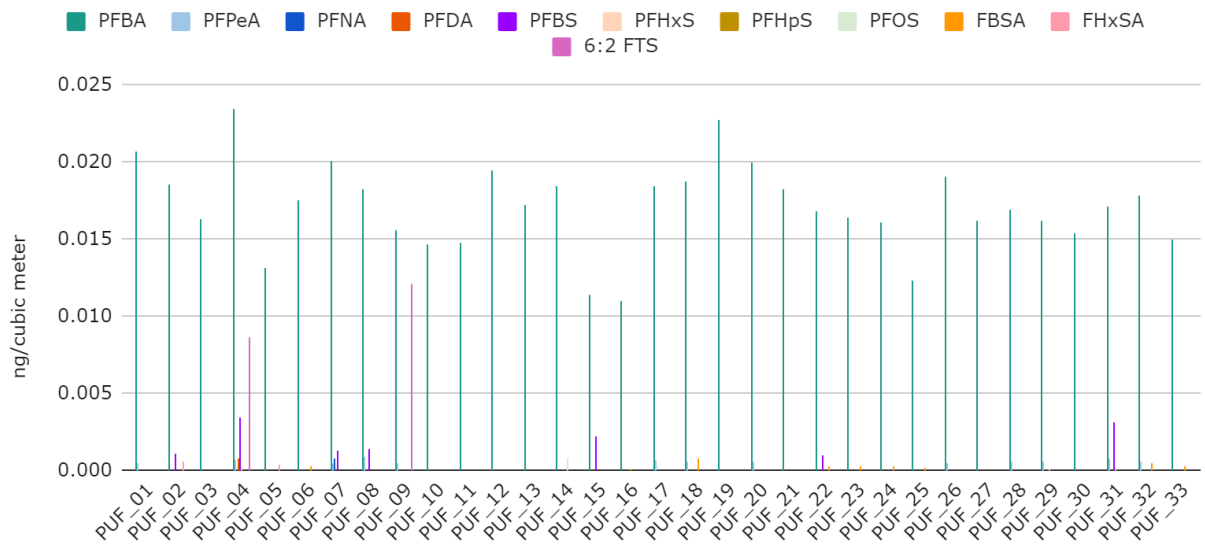


Figure 7: Calculated concentrations of ionic PFAS compounds in the PUF disc samples reported in ng/m^3.

Figure 7 shows the calculated concentrations of ionic PFAS compounds in PUF disc samplers, reported as ng per cubic meter of air. Concentrations were calculated using the sampling rate provided by Ahrens et al., *2013.*

It is clear from Figure 6 that PFBA is the most abundant ionic PFAS compound found in the PUF discs above the limits of detection. However, even though measured concentrations passed the QAQC, and samples were around 10x higher than blanks, there should be further consideration of whether PFBA is truly present in air, especially as we cannot see similar levels of PFBA in the air samplers.

Summary

Overall, the combination of air samplers and PUF samplers captured several target compounds, both ionic and volatile PFAS. To put the results into perspective for those compounds above detection limits, results are compared to that of previous studies, both indoor and outdoor environments.

There is no published data for the use of air samplers in measuring PFAS concentrations in outdoor settings or for the combination of PUF and air samplers. However, there are published data for the use of a) air samplers (alongside PE sheets) indoors for measuring PFAS, b) the use of PUF discs to measure PFAS concentrations outdoors, and c) the use of other sampling methods to measure PFAS concentrations outdoors. All of which may be helpful comparisons for the data collected in this study.

Ahrens et al., *2013*, deployed passive air PUF samplers for various lengths of time at a semi-urban meteorological station in Toronto. They reported average concentrations of 0.24, 0.13, and 0.96 pg m^{-3} for PFBS, PFHxS, and PFOS respectively using the PUF disc samplers. Results for PFAS above detection limits based on the PUF samplers show averages of 1.96, 0.16, and 0.81 pg m^{-3} for PFBS, PFHxS, and PFOS respectively.

Wang et al. *2021*, conducted a study to measure the PFAS air concentrations within a 20 km radius of a fluorochemical industry park in China, reporting a mean sum concentration of 2729 pg m^{-3} for 12 ionic PFAS compounds. The mean PFBA concentration for the 20 km radius was 459 pg m^{-3}, around 25x the mean PFBA concentration detected in MI. The compound with highest concentration measured by Wang et al. *2021*, was PFOA, with a mean of 1610 pg m^{-3}. PFOA was only detected in 3 locations in MI, with an average of 400 pg m^{-3} across those 3 sites. This is around 4x less than detected in an area with a known PFAS source.

A study published by Morales-McDevitt et al., *2021*, reported volatile PFAS air concentrations for indoor environments, including an outdoor clothing store in California. In this environment, 8:2 FTOH dominated with an average concentration of 200 ng m^{-3}. 6:2 FTOH and 10:2 FTOH were also detected with average concentrations of 70 ng m^{-3} and 30 ng m^{-3}. A direct comparison between studies is difficult as the data reported by Morales-McDevitt et al. is blank corrected (blank average subtracted from samples), but still 10-100x higher than concentrations reported for outdoor air in MI.

In summary, the measured concentrations in this study were similar to those detected in other outdoor semi-urban areas and much lower than those detected in outdoor environments within proximity to known sources. In comparison to recently reported indoor concentrations, the outdoor PFAS concentrations measured in this study were much lower.

The combined use of air samplers and PUF discs seems suitable for measuring both ionic and volatile PFAS compounds in outdoor environments. However, even with the large number of non detects and relatively low air concentrations (as compared to other studies), this data alone may not provide the entire picture of PFAS air concentrations in MI. Future studies may include looking at seasonal variation in air concentrations (for instance, a deployment in the same locations during summer or warmer temperatures), or measuring concentrations at different locations. A few possibilities for alternate locations could include areas with known high concentrations of PFAS in the water or soil, or in areas where there is a known point source of PFAS contamination. Longer deployment times would help overcome limits of detection.

Acknowledgements
We thank MPART (EGLE) and EGLE's Air Quality Division for their contribution to the project, including the deployment and collection of the samplers.

References

Ahrens, L.; Harner, T.; Shoeib, M.; Koblizkova, M.; Reiner, E. J. Characterization of Two Passive Air Samplers for per- and Polyfluoroalkyl Substances. *Environmental Science & Technology* **2013**, *47* (24), 14024–14033.

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Wang, P.; Zhang, M.; Li, Q.; Lu, Y. Atmospheric Diffusion of Perfluoroalkyl Acids Emitted from Fluorochemical Industry and Its Associated Health Risks. *Environment International* **2021**, *146*, 106247.

Appendix A- Figures

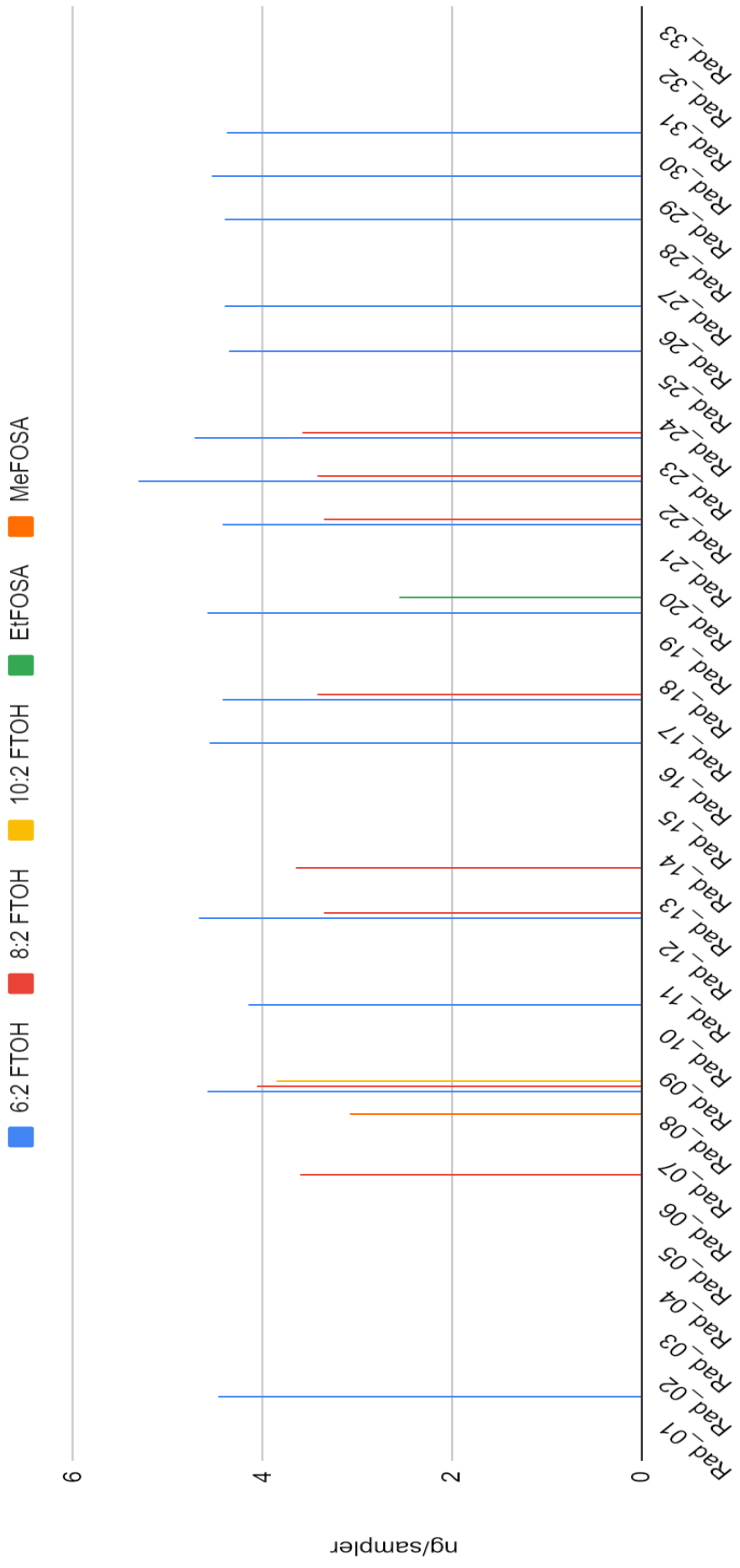


Figure 2: Measured volatile PFAS compounds in the air samplers reported in ng/sampler.

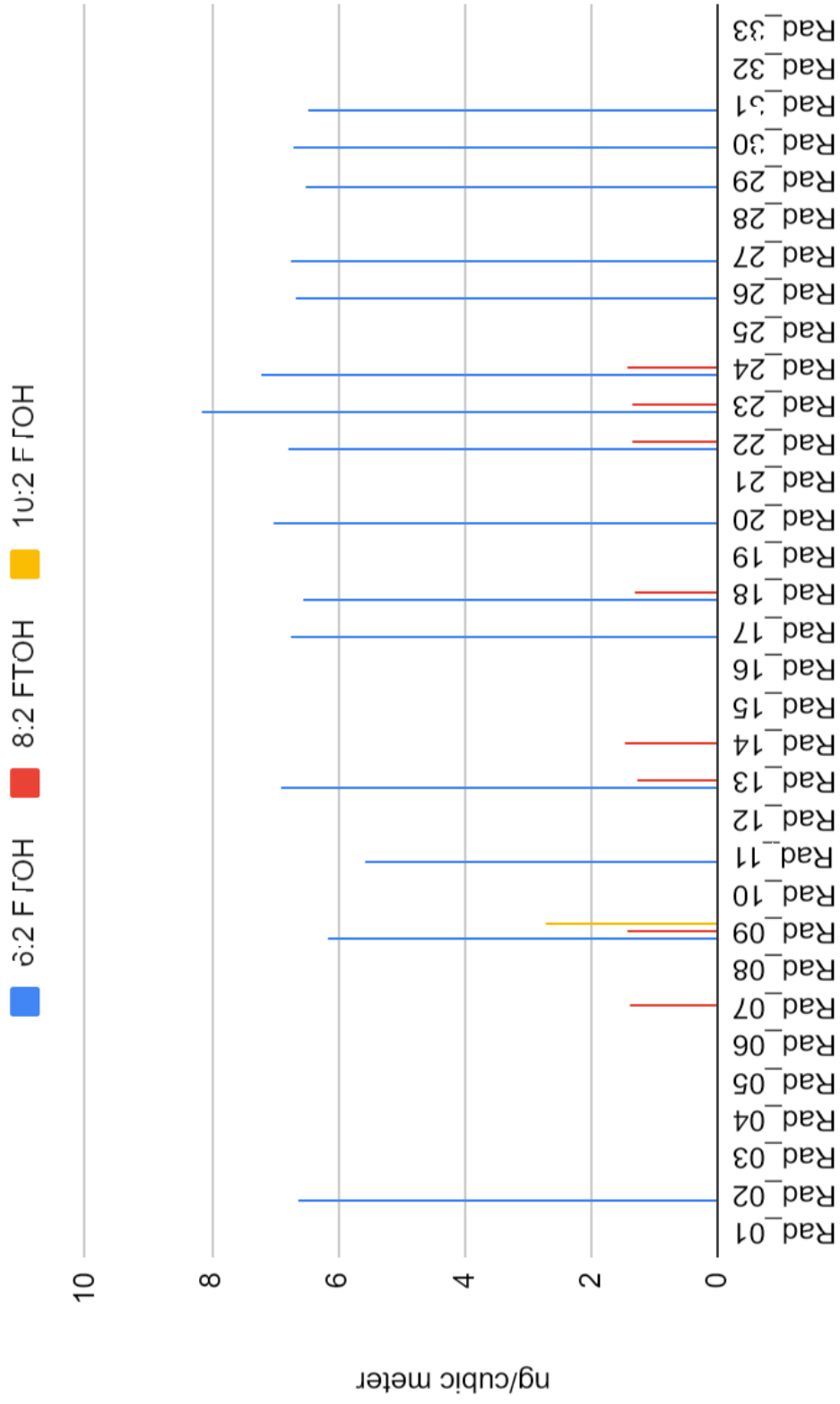


Figure 3: Calculated concentrations of volatile PFAS compounds in the air samplers reported in ng/m^3. Calculated concentrations for EtFOSA and MeFOSA are not reported as no sampling rate is available.

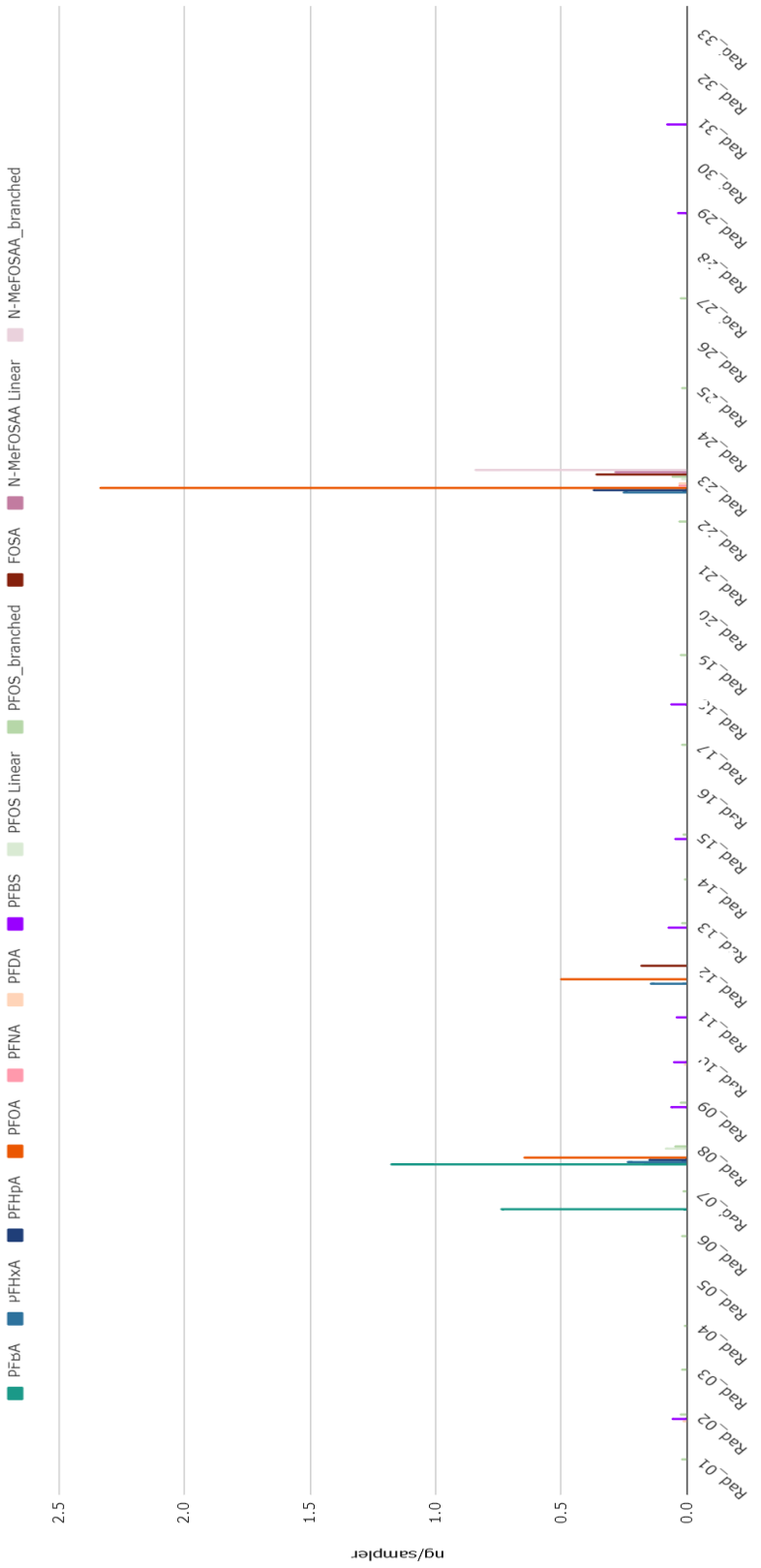
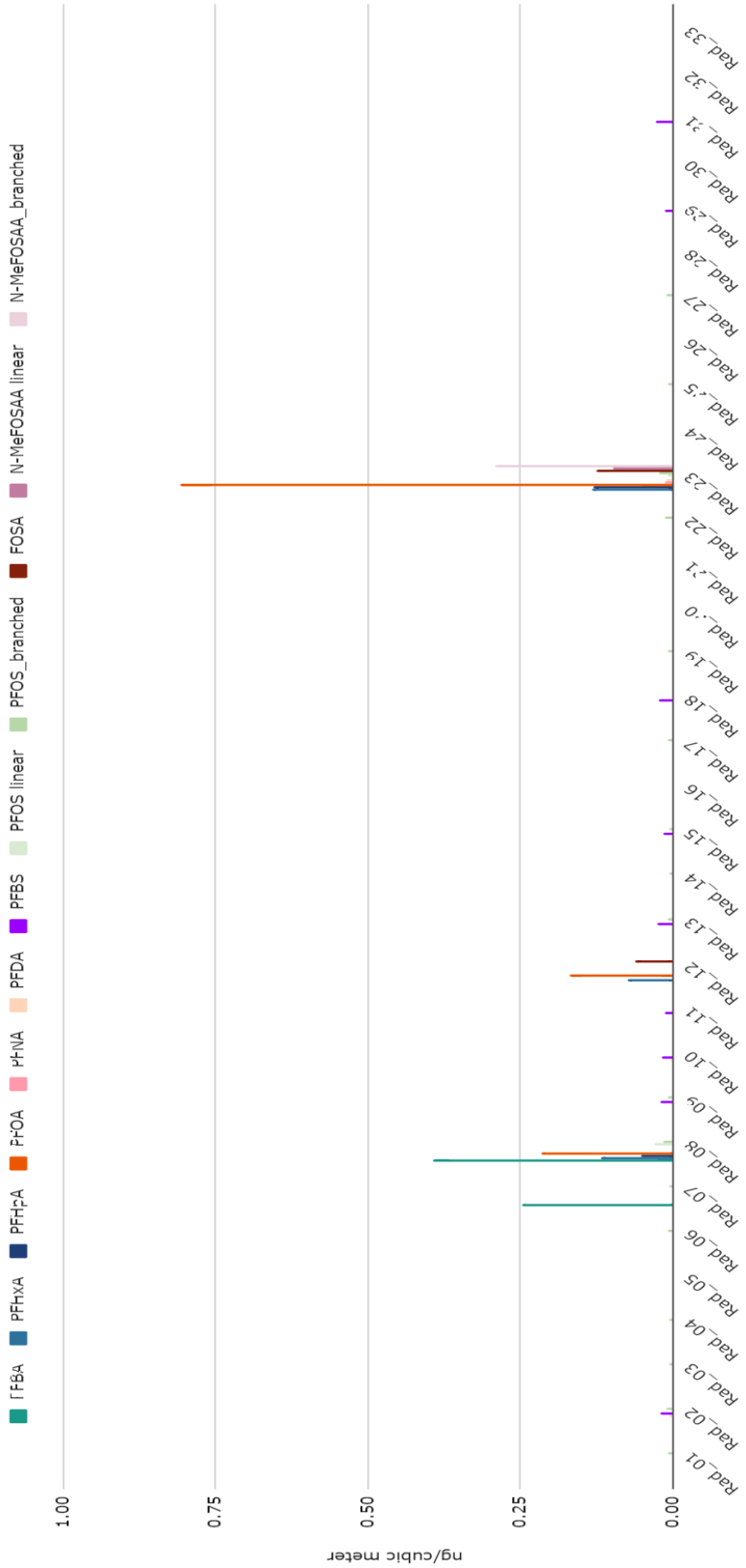


Figure 4: Measured concentrations of ionic PFAS compounds in the air samplers reported in ng/sampler.



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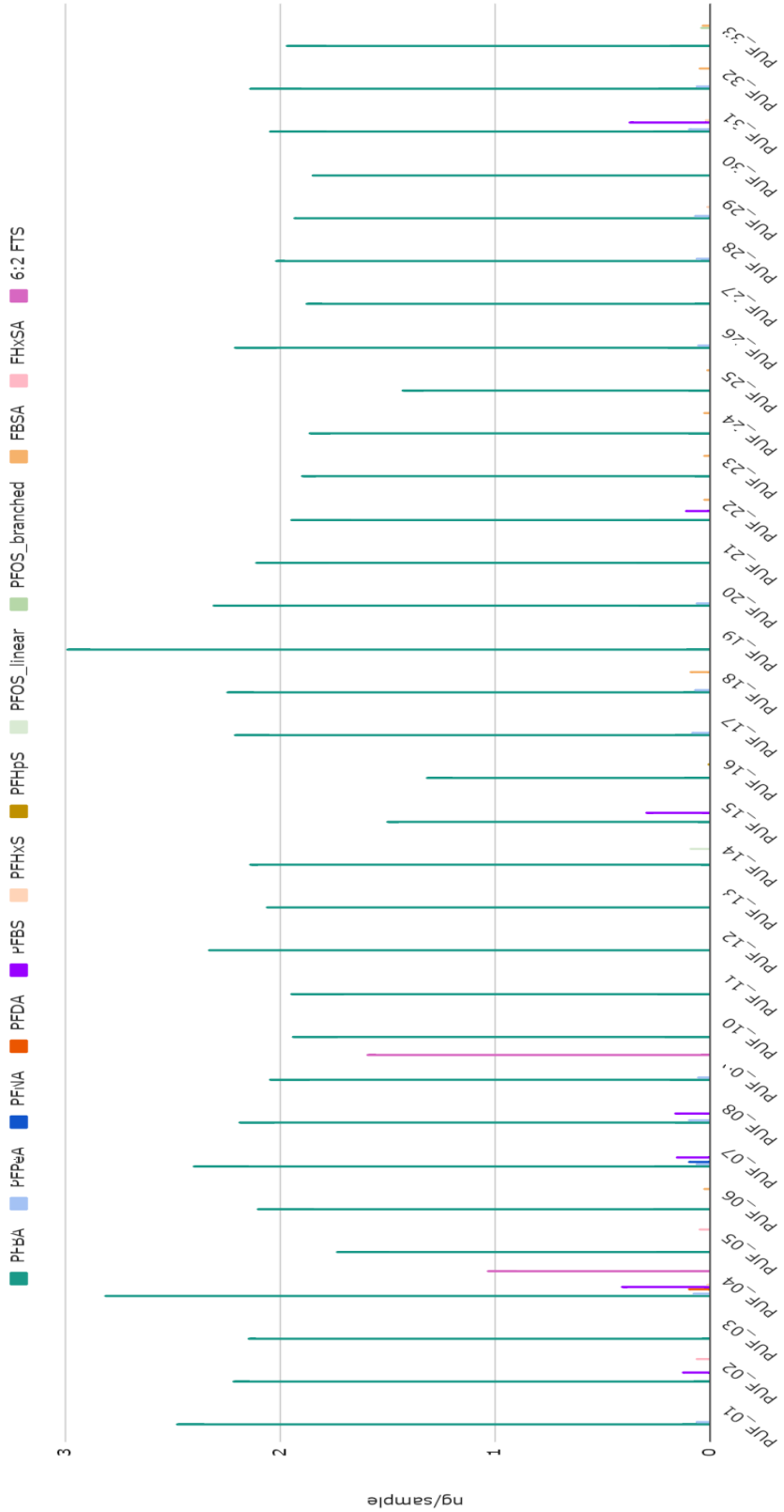
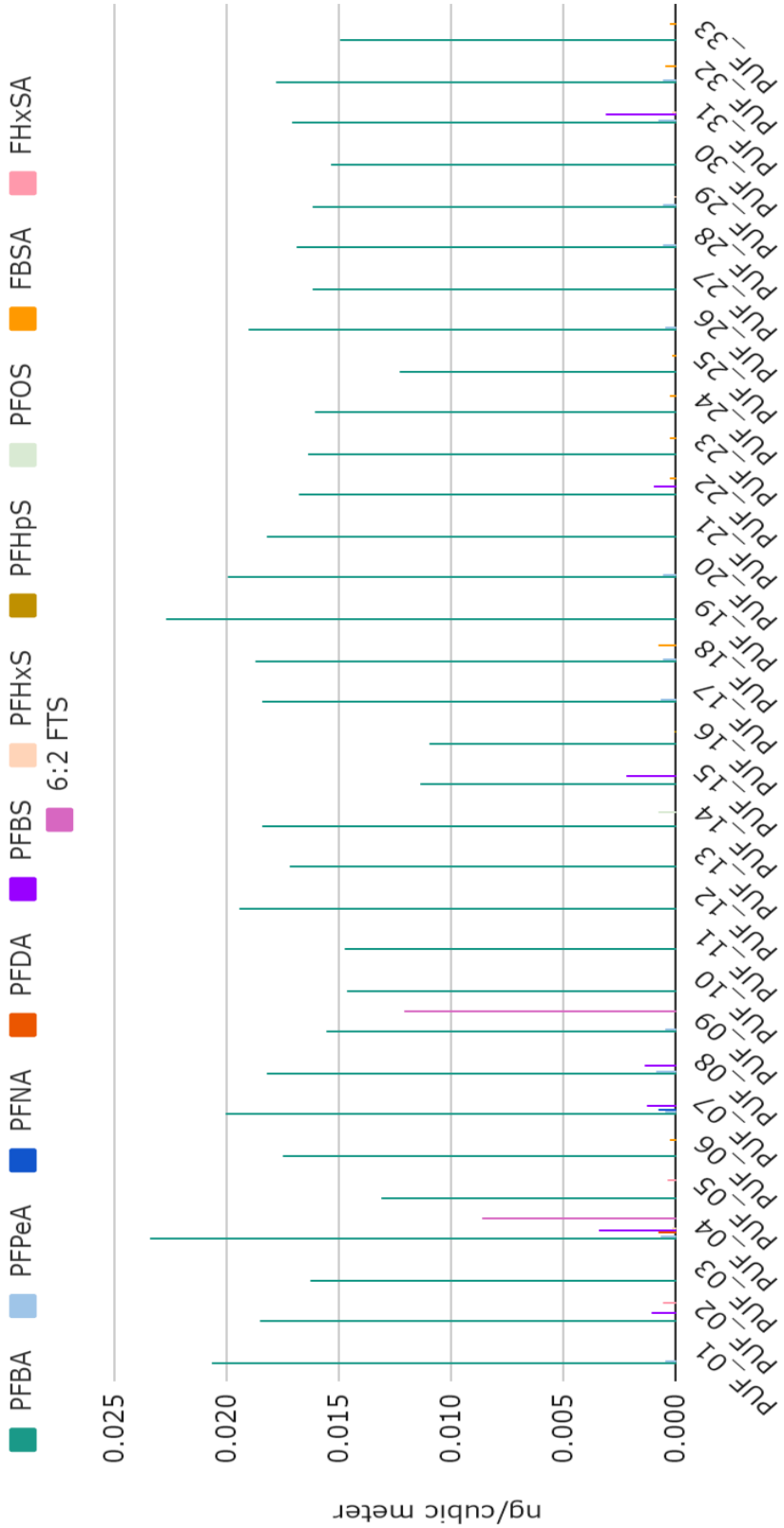


Figure 6: Measured concentrations of ionic PFAS compounds in the PUF disc samples reported in ng/sample.



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